

Title: DEVELOPMENT OF HIGH ACTIVITY, COAL-DERIVED, PROMOTED
CATALYTIC SYSTEMS FOR NO_x REDUCTION AT LOW TEMPERATURES

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ABSTRACT

OBJECTIVES

This project is directed at an investigation of catalytic NO_x reduction mechanisms on coal-derived, activated carbon supports at low temperatures (300°C-450°C). Promoted carbon systems offer some potentially significant advantages for heterogeneous NO_x reduction. These include: low cost; high activity at low temperatures, to minimize carbon loss; oxygen resistance; and a support material which can be engineered with respect to porosity, transport and catalyst dispersion characteristics.

The project is currently focused on two promising systems - potassium; and Co/Ni-rare earth oxide-Pt, which have both been shown to be effective for NO reduction at low temperatures, with low carbon loss. In particular, the focus is on the investigation of : (1) a novel, "two-stage" process for the complete reduction of NO to N₂ and O₂ *via* N₂O as an intermediate; and (2) the use of H₂ and CO reducing agents in conjunction with the promoted carbon systems.

In order to develop and optimize these approaches, however, the fundamental mechanisms responsible for NO_x reduction in these catalytic systems must be better understood and quantified. In this regard, various techniques that have been developed in our laboratory to investigate carbon reactivity will be applied to accomplish this objective. These include temperature programmed reaction (TPR), and post-reaction/chemisorption temperature programmed desorption (TPD) methods.

ACCOMPLISHMENTS TO DATE

Apparatus: (1) A MS-TGA (mass spectrometric-thermogravimetric analysis) apparatus was modified to the requirements of this project. A NO_x chemiluminescence analyzer was added to monitor NO_x concentrations in the feed and product streams. In addition, the computer control and data acquisition system has been updated and modified to accommodate the specific types of experiments required. (2) A packed bed reactor/gas flow system was constructed for performing reactivity studies. This system employs a gas calibration/mixing system for varying feed composition to the packed bed, a NO_x chemiluminescence analyzer, and a quadrupole mass spectrometer. This system is used for steady-state reactivity studies, as well as temperature programmed reaction/desorption studies of the effects of gas composition on intermediate oxygen surface complex populations on carbon substrates.

Experimental Program: Both systems have been used to investigate the effects of NO and CO in the gas phase on intermediate oxygen surface complex populations on carbonaceous substrates. These studies are intended to establish the mechanism of gas phase reducing agents on heterogeneous NO reduction.

Work has also been focused on N₂O reduction on phenolic resin chars, and the same chars doped with potassium catalyst.

Work has also continued on the application of small angle scattering to the characterization of porosity and porosity evolution of carbons subjected to NO and other oxidants. This includes both contrast matching, small angle neutron scattering, and small angle X-ray scattering at the Advanced Photon Source (APS) at the Argonne National Laboratory. In particular, the latter studies are directed at measurements of “real time” evolution of porosity in these materials. These techniques are being applied for porosity characterization of the carbon support materials for NO_x reduction systems.

ARTICLES, PRESENTATIONS, AND STUDENT SUPPORT

Journal Articles (peer reviewed)

- Hall, P.J., Antxustegi, M.M., and Calo, J.M., "Development of Porosity in Pittsburgh No. 8 Coal Char As Investigated by Contrast-Matching Small Angle Neutron Scattering and Gas Adsorption Techniques," *Energy & Fuels*, **12**, 542-546, 1998.
- Antxustegi, M.M., Hall, P.J., and Calo, J.M., "The Use of Contrast Matching Small Angle Neutron Scattering Techniques to Monitor Closed Porosity in Carbons," *J. Coll. Intf. Sci.* **202**, 490-498, 1998.
- Calo, J.M., Suuberg, E.M., Aarna, I., Linares-Solano A., Salinas-Martínez de Lecea, C., and M.J. Illán-Gómez, M.J., "The Role of Surface Area in the NO-Carbon Reaction," *Energy & Fuels* **13**, 761-762, 1999.
- Hall, P.J., Brown, S.D., and Calo, J.M., "The Pore Structure of the Argonne Coals as Interpreted From Contrast Matching Small Angle Neutron Scattering," *Fuel*, in press, 2000.
- Hall, P.J., Brown, S.D., Fernandez, J., and Calo, J.M., "The Effects of the Electronic Structure of Micropores on the Small Angle Scattering of X-Rays and Neutrons," *Carbon*, in press, 2000.

Conference Presentations

- Calo, J.M., Hall, P.J., Brown, S., Fernandez, J., and Antxustegi, M., "Carbon Porosity Development Via Small Angle Scattering," Proc. Carbon '99 - 24th Biennial Conf. Carbon, Charleston, SC, p. 440, 1999.
- Calo, J.M., Hall, P.J., Brown, S., Fernandez, J., and Antxustegi, M., "Carbon Porosity Characterization Via Small Angle Neutron Scattering," to be presented at "Characterization of Porous Materials: From Angstroms to Millimeters," 2nd International TRI/Princeton Workshop, June, 2000.
- Calo, J.M., Hall, P.J., Brown, S.D., and Winans, R.E., "Real Time Determination of Porosity Development in Carbons using SAXS," to be presented at Eurocarbon 2000, 1st World Conference on Carbon, Berlin, July, 2000.

Students Supported Under This Grant

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